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(71) Applicant (*for all designated States except US*): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): HALL, Robin, Gibson [GB/GB]; 27 Blackfriars Court, Stowell Street, Newcastle upon Tyne NE1 4XB (GB).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).

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(54) Title: DETERGENT COMPOSITIONS

(57) Abstract

There is provided a detergent composition suitable for use in laundry and dish washing methods, comprising a cationic ester surfactant and a alkalinity system and wherein a means is provided for delaying the release of said alkalinity system relatively to the release of said cationic ester surfactant.

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Detergent compositions

Technical field

The present invention relates to detergent compositions comprising a cationic ester surfactant and an alkalinity system, wherein is provided a means to delay the release of the alkalinity system to the wash solution.

Background to the invention

The satisfactory removal of greasy soils/stains, that is soils/stains having a high proportion of triglycerides or fatty acids, is a challenge faced by the formulator of detergent compositions for use in machine laundry and dishwashing methods. Surfactant components have traditionally been employed in detergent products to facilitate the removal of such greasy soils/stains. In particular, surfactant systems comprising cationic esters have been described for use in greasy soil/stain removal.

For example, EP-B-21,491 discloses detergent compositions containing a nonionic/cationic surfactant mixture and a builder mixture comprising aluminosilicate and polycarboxylate builder. The cationic surfactant may be a cationic ester. Improved particulate and greasy/oily soil removal is described.

US-A-4,228,042 discloses biodegradable cationic surfactants, including cationic ester surfactants for use in detergent compositions to provide greasy/oily soil removal. The combination of these cationic surfactants with nonionic surfactants in compositions designed for particulate soil removal is also described. Anionic surfactants are disclosed as optional components of the compositions, but are present at low levels relative to the cationic surfactant component.

US-A-4,239,660 discloses laundry detergent compositions containing cationic ester surfactant and nonionic surfactant at defined weight ratios

and an high alkalinity source. The alkalinity source enables a wash solution having a pH of from 8 to 10 to be formed within 3 minutes of dissolution of the composition in water at 100°F (37°C) at a solution concentration of 0.15%. This is achieved by the use of highly soluble alkalinity sources.

US-A-4,260,529 discloses laundry detergent compositions having a pH of no greater than 11 containing cationic ester surfactant and nonionic surfactant at defined weight ratios. Anionic surfactants are disclosed as optional components of the compositions, but are present at low levels relative to the cationic ester surfactant component.

The Applicants have now found that a problem with the use of certain cationic ester surfactants is the tendency for the ester linkage to hydrolytically cleave, thereby breaking up the surfactant molecule, under the wash conditions of a typical laundry or dishwashing method and under the typical alkalinity conditions of such laundry and dishwashing methods employing cationic surfactants. Precisely the high alkalinity sources, taught by the prior art to be essential for the optimal surfactant performance of the cationic ester surfactants, can be the cause of the hydrolytic cleavage of the ester linkage, which can compromise the surfactant performance in the wash.

It has now been found that a solution to this problem is provided when the cationic ester surfactant is employed in a detergent composition providing a means to delay the release or establishment of the alkalinity in the wash solution. Such a means provides a reduced alkalinity at the beginning of the wash and thereby an overall reduction or delay of the hydrolytic cleavage of the ester linkage is achieved during the wash. Overall, sufficient alkalinity is delivered to the wash to allow the cationic ester surfactant to perform optimal greasy soil/ stain removal during the wash. Thus, introduction of such a means in a detergent composition will optimise the overall surfactant performance in the wash.

All documents cited in the present description are, in relevant part, incorporated herein by reference.

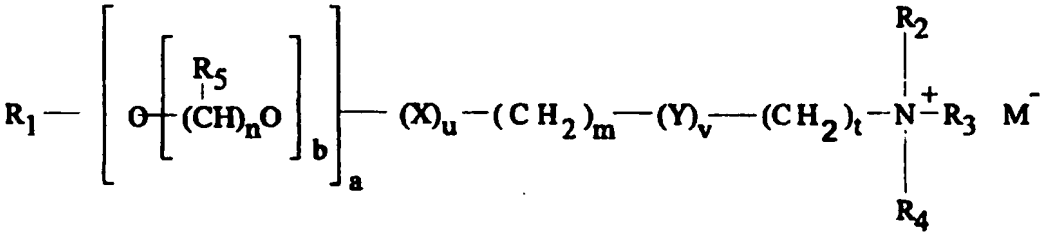
Summary of the Invention

According to the present invention there is provided a detergent composition containing

(a) a cationic ester surfactant; and
(b) an alkalinity system,

wherein a means is provided for delaying the release to a wash solution of said alkalinity system relative to the release of said cationic ester surfactant such that in the T50 test method herein described the time to achieve a concentration that is 50% of the ultimate concentration of said cationic ester surfactant is at least 120 seconds less than the time to achieve a concentration that is 50% of the ultimate concentration of said alkalinity system.

In a preferred aspect, the cationic ester surfactant is selected from those having the formula:



wherein R_1 is a C_5-C_{31} linear or branched alkyl, alkenyl or alkaryl chain or $M^- N^+(R_6R_7R_8)(CH_2)_s$; X and Y, independently, are selected from the group consisting of COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCO, OCOO, OCONH or NHCOO group; R_2, R_3, R_4, R_6, R_7, and R_8 are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl, hydroxy-alkenyl and alkaryl groups having from 1 to 4 carbon atoms; and R_5 is independently H or a C_1-C_3 alkyl group; wherein the values of m, n, s and t independently lie in the range of from

0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion.

The alkalinity system preferably comprises alkaline salts selected from the group consisting of alkali metal or alkaline earth carbonate, bicarbonate, hydroxide or silicate salts, crystalline layered silicate and inorganic perhydrate salts and any mixtures thereof.

Detailed description of the invention

Cationic ester surfactant

An essential element of the detergent compositions of the invention is a cationic ester surfactant preferably present at a level from 0.1% to 20.0%, more preferably from 0.5% to 10%, most preferably from 1.0% to 5.0% by weight of the detergent composition.

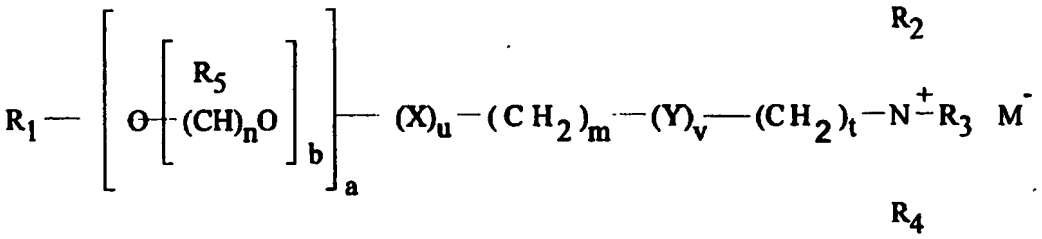
The cationic ester surfactant of the present invention is a, preferably water dispersible, compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group.

Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

In one preferred aspect the ester linkage and cationically charged group are separated from each other in the surfactant molecule by a spacer group consisting of a chain comprising at least three atoms (i.e. of three atoms chain length), preferably from three to eight atoms, more preferably from three to five atoms, most preferably three atoms. The atoms forming the spacer group chain are selected from the group consisting of carbon, nitrogen and oxygen atoms and any mixtures thereof, with the proviso that any nitrogen or oxygen atom in said chain connects only with carbon atoms in the chain. Thus spacer groups

having, for example, -O-O- (i.e. peroxide), -N-N-, and -N-O- linkages are excluded, whilst spacer groups having, for example $-CH_2-O-CH_2-$ and $-CH_2-NH-CH_2-$ linkages are included. In a preferred aspect the spacer group chain comprises only carbon atoms, most preferably the chain is a hydrocarbyl chain.

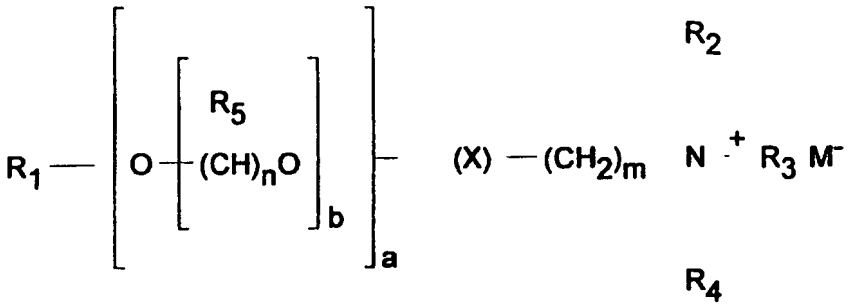
Preferred cationic ester surfactants are those having the formula:



wherein R_1 is a C_5-C_{31} linear or branched alkyl, alkenyl or alkaryl chain or M^-. $N^+(R_6R_7R_8)(CH_2)_s$; X and Y, independently, are selected from the group consisting of COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCO, OCOO, OCONH or NHCOO group; R_2, R_3, R_4, R_6, R_7, and R_8 are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl and hydroxy-alkenyl groups having from 1 to 4 carbon atoms and alkaryl groups; and R_5 is independently H or a C_1-C_3 alkyl group; wherein the values of m, n, s and t independently lie in the range of from 0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion.

Preferably M is selected from the group consisting of halide, methyl sulfate, sulfate, and nitrate, more preferably methyl sulfate, chloride, bromide or iodide.

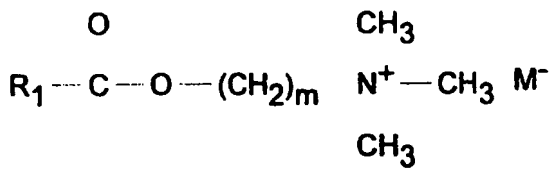
In a preferred aspect, the cationic ester surfactant is selected from those having the formula:



wherein R_1 is a C_5-C_{31} linear or branched alkyl, alkenyl or alkaryl chain; X is selected from the group consisting of COO, OCO, OCOO, OCONH and NHCOO; R_2, R_3, and R_4 are independently selected from the group consisting of alkyl and hydroxyalkyl groups having from 1 to 4 carbon atoms; and R_5 is independently H or a C_1-C_3 alkyl group; wherein the value of n lies in the range of from 0 to 8, the value of b lies in the range from 0 to 20, the value of a is either 0 or 1, and the value of m is from 3 to 8.

More preferably R_2, R_3 and R_4 are independently selected from a C_1-C_4 alkyl group and a C_1-C_4 hydroxyalkyl group. In one preferred aspect at least one, preferably only one of R_2, R_3 and R_4 is a hydroxyalkyl group. The hydroxyalkyl preferably has from 1 to 4 carbon atoms, more preferably 2 or 3 carbon atoms, most preferably 2 carbon atoms. In another preferred aspect at least one of R_2, R_3 and R_4 is a C_2-C_3 alkyl group, more preferably two C_2-C_3 alkyl groups are present.

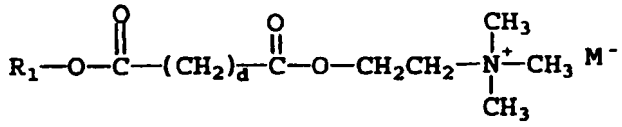
Highly preferred water dispersible cationic ester surfactants are the esters having the formula:

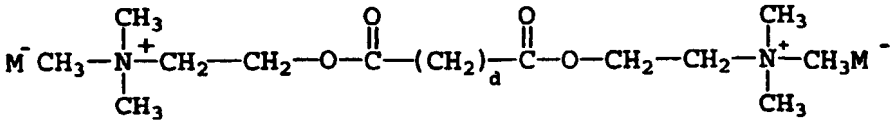


where m is from 1 to 4, preferably 2 or 3 and wherein R_1 is a C_{11}-C_{19} linear or branched alkyl chain.

Particularly preferred choline esters of this type include the stearoyl choline ester quaternary methylammonium halides ($R^1=C_{17}$ alkyl), palmitoyl choline ester quaternary methylammonium halides ($R^1=C_{15}$ alkyl), myristoyl choline ester quaternary methylammonium halides ($R^1=C_{13}$ alkyl), lauroyl choline ester methylammonium halides ($R^1=C_{11}$ alkyl), cocoyl choline ester quaternary methylammonium halides ($R^1=C_{11}$-C_{13} alkyl), tallowyl choline ester quaternary methylammonium halides ($R^1=C_{15}$-C_{17} alkyl), and any mixtures thereof.

Other suitable cationic ester surfactants have the structural formulas below, wherein d may be from 0 to 20.





In a preferred aspect the cationic ester surfactant is hydrolysable under the conditions of a laundry wash method.

The particularly preferred choline esters, given above, may be prepared by the direct esterification of a fatty acid of the desired chain length with

dimethylaminoethanol, in the presence of an acid catalyst. The reaction product is then quaternized with a methyl halide, preferably in the presence of a solvent such as ethanol, water, propylene glycol or preferably a fatty alcohol ethoxylate such as C_{10}-C_{18} fatty alcohol ethoxylate having a degree of ethoxylation of from 3 to 50 ethoxy groups per mole forming the desired cationic material. They may also be prepared by the direct esterification of a long chain fatty acid of the desired chain length together with 2-haloethanol, in the presence of an acid catalyst material. The reaction product is then quaternized with trimethylamine, forming the desired cationic material.

Alkalinity system

Another essential aspect of the detergent composition of the present invention is an alkalinity system, comprising components capable of providing alkalinity species in solution. By alkalinity species it is meant for the purposes of this invention: carbonate, bicarbonate, hydroxide, the various silicate anions, inorganic perhydrate anions and crystalline layered silicates. Such alkalinity species can be formed for example, when alkaline salts selected from alkali metal or alkaline earth carbonate, bicarbonate, hydroxide or silicate salts, crystalline layered silicate or inorganic perhydrate salts, preferably alkali metal percarbonate, perborate and persilicate salts and any mixtures thereof, are dissolved in water.

Preferably, the alkaline earth and alkali metal carbonates and bicarbonates are selected from sodium carbonate, potassium carbonate, sodium bicarbonate and potassium bicarbonate and mixtures thereof, and including sodium carbonate, sesqui-carbonate and any mixtures thereof with ultra-fine calcium carbonate such as are disclosed in German Patent Application No. 2,321,001 published on November 15, 1973. Suitable mixtures include mixtures of sodium carbonate with sodium bicarbonate, sodium carbonate with potassium carbonate and sodium carbonate with sodium bicarbonate and potassium carbonate. More preferably, the alkalinity system is substantially free from carbonate salts, but may comprise bicarbonate salts.

The carbonate and bicarbonate preferably have a amorphous structure. Preferably the carbonate and bicarbonates are coated with coating materials, described below in the section 'delayed rate of release - means'.
The particles of carbonate and bicarbonate can have a mean particle size of 250μm or greater, preferably 500μm or greater. It is preferred that fewer than 20% of the particles have a particle size below 500μm.

The mean particle size of the particles of carbonate and bicarbonate herein is determined by reference to a method involving choice of varied sizes of sieve through which the sample is attempted to be passed. The mean particle size of a sample is given by the diameter of sieve through which half of the mass of the sample will pass, and accordingly through which half of the sample will not pass.

Suitable silicates include the sodium silicates with an SiO_2: Na_2O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.0 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO_2: Na_2O ratio of 2.0 is the most preferred silicate. Preferably the silicates have an amorphous structure.

Alkali metal percarbonate salts are also suitable alkalinity species and are described in more detail in the section 'inorganic perhydrate salts' herein. The alkali metal percarbonate used may preferably be sodium percarbonate or potassium percarbonate, more preferably sodium percarbonate. The percarbonate is generally in particulate form. The percarbonate particles generally have a mean particle diameter of 150-1200μm, preferably 500-900μm. Preferably, the particles of percarbonate are coated. Alkali metal persilicates, as described in the section 'inorganic perhydrate salts', are also suitable alkalinity species.

Another suitable alkalinity species include a crystalline layered silicate, preferably a crystalline δ-layered silicate, and most preferably the crystalline δ-layered silicate is a crystalline δ-layered sodium silicate with the general formula

$NaMSi_xO_{2+1} .yH_2O$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. The most preferred material is δ-$Na_2Si_2O_5$, available from Hoechst AG as NaSKS-6.

The crystalline layered silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionisable material. The solid, water-soluble ionisable material is selected from organic acids, organic and inorganic acid salts and mixtures thereof. In accord with the invention, the crystalline layered silicate alkalinity species is preferably coated with a coating material such as citric acid, as described in the section 'delayed release-means'.

The alkalinity system is preferably present in an amount of from 1% to 75%, more preferably in an amount of from 10% to 40% by weight of the detergent composition.

Relative release kinetics

An essential aspect of the invention is a means, which is provided for delaying the release to a wash solution of the alkalinity system relative to the release of the cationic ester surfactant.

Delayed rate of release - means

The means preferably provide for delayed release of the alkalinity system itself to the wash solution. The delayed release means can include coating any suitable alkalinity species with a coating designed to provide the delayed release. The coating may therefore, for example, comprise a poorly water soluble material, or be a coating of sufficient thickness that the kinetics of dissolution of the thick coating provide the controlled rate of release.

The coating material may be applied using various methods. Any coating material is typically present at a weight ratio of coating material to alkalinity species of from 1:99 to 1:2, preferably from 1:49 to 1:9.

Suitable coating materials include triglycerides (e.g. partially) hydrogenated vegetable oil, soy bean oil, cotton seed oil) mono or diglycerides, microcrystalline waxes, gelatin, cellulose, fatty acids and any mixtures thereof.

Other suitable coating materials can comprise the alkali and alkaline earth metal sulphates. An other suitable coating material can comprise citric acid.

A preferred coating material is sodium silicate of SiO_2 : Na_2O ratio from 1.6 : 1 to 3.4 : 1, preferably 2.8 : 1, applied as an aqueous solution to give a level of from 2% to 10%, (normally from 3% to 5%) of silicate solids by weight of the percarbonate. Magnesium silicate can also be included in the coating.

Other suitable coating materials for use herein include polymers derived from amino acids such as polyglutamine acid, as disclosed in GB 91-

20653.2, and polyaspartic acid, as disclosed in EP 305 282, and EP 351 629. EP-A-0382464 discloses coating materials such as polyacrylic acid and cellulose acetate phthalate. These polymeric coating materials are water-soluble (acidic) polymers which are preferably used as coating material for inorganic perhydrate salts and peroxyacid bleach precursors.

Suitable polymers for use herein have a molecular weight in the range of from 1000 to 280,000, preferably from 1500 to 150,000. Preferably, the polymers have a melting point superior to 30°C.

Any coating materials may be combined with organic binder materials to provide composite inorganic salt/organic binder coatings. Suitable binders include the C_{10}-C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole of alcohol and more preferably the C_{15}-C_{20} primary alcohol ethoxylates containing from 20 - 100 moles of ethylene oxide per mole of alcohol.

Other preferred binders include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000 and polyethylene glycols (PEG) with an average molecular weight of from 600 to 10,000 are examples of such polymeric materials. Copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the polymer are further examples of polymeric materials useful as binder agents. These polymeric materials may be used as such or in combination with solvents such as water, propylene glycol and the above mentioned C_{10}-C_{20} alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole. Further examples of binders include the C_{10}-C_{20} mono- and diglycerol ethers and also the C_{10}-C_{20} fatty acids.

Cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts are other examples of binders suitable for use herein.

One method for applying the coating material involves agglomeration. Preferred agglomeration processes include the use of any of the organic binder materials described hereinabove. Any conventional

agglomerator/mixer may be used including, but not limited to pan, rotary drum and vertical blender types. Molten coating compositions may also be applied either by being poured onto, or spray atomized onto a moving bed of bleaching agent. Preferred methods for applying coating materials are described in WO 93/ 918259.

Other means of providing the required delayed release include mechanical means for altering the physical characteristics of the alkalinity system to control its solubility and rate of release. Suitable means could include compaction, mechanical injection, manual injection.

Another means to delay the alkalinity release can include a suitable choice of alkalinity species with an amorphous structure. These are known to dissolve relatively slowly in comparison to alkalinity species with a crystalline structure. Thus, a suitable choice of amorphous alkalinity species will provide a delay of alkalinity release.

Additionally, a means of delayed release may include a suitable choice of any other components of the detergent composition matrix such that when the composition is introduced to the wash solution the ionic strength environment therein provided enables the required delayed release kinetics to be achieved.

Relative rate of release - kinetic parameters

The release of the cationic ester surfactant relative to that of the alkalinity system is such that in the T50 test method herein described the time to achieve a concentration that is 50% of the ultimate concentration of the cationic ester surfactant is at least 120 seconds less than the time to achieve a concentration of that is 50% of the ultimate concentration of said alkalinity system.

Preferably, the time to achieve a concentration that is 50% of the ultimate concentration of the cationic ester surfactant is more than 300 seconds less than the time to achieve a concentration that is 50% of the ultimate concentration of the alkalinity system.

Delayed release - test method

The delayed release kinetics herein are defined with respect to a 'TA test method' which measures the time to achieve A% of the ultimate concentration/level of that component when a composition containing the component is dissolved according to the standard conditions now set out.

The standard conditions involve a 1 litre glass beaker filled with 1000 ml of distilled water at 20°C, to which 10g of composition is added. The contents of the beaker are agitated using a magnetic stirrer set at 100 rpm. The ultimate concentration/level is taken to be the concentration/level attained 15 minutes after addition of the composition to the water-filled beaker.

Suitable analytical methods are chosen to enable a reliable determination of the incidental, and ultimate in solution concentrations of the component of concern, subsequent to the addition of the composition to the water in the beaker.

Such analytical methods can include those involving a continuous monitoring of the level of concentration of the component, including for example photometric and conductimetric methods.

Alternatively, methods involving removing titres from the solution at set time intervals, stopping the dissolution process by an appropriate means such as by rapidly reducing the temperature of the titre, and then determining the concentration of the component in the titre by any means such as chemical titrimetric methods, can be employed.

Suitable graphical methods, including curve fitting methods, can be employed, where appropriate, to enable calculation of the the TA value from raw analytical results.

The particular analytical method selected for determining the concentration of the component, will depend on the nature of that component, and of the nature of the composition containing that component.

Additional detergent components

The detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the precise nature of the washing operation for which it is to be used.

The compositions of the invention preferably contain one or more additional detergent components selected from additional surfactants, bleaches, builders, organic polymeric compounds, enzymes, suds suppressors, lime soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors.

Additional surfactant

The detergent compositions of the invention preferably contains one or more additional surfactants selected from anionic, nonionic, non-ester cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Where present, ampholytic, amphoteric and zwitteronic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Anionic surfactant

A preferred additional component of the detergent composition of the invention is an anionic surfactant. Essentially any anionic surfactants useful for detersive purposes are suitable. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

The weight ratio of anionic surfactant to cationic ester surfactant in the surfactant system is from 3:1 to 15:1, preferably from 4:1 to 12:1, most preferably from 5:1 to 10:1.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5-C_{17} acyl-N-(C_1-C_4 alkyl) and -N-(C_1-C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C_{10}-C_{18} alkyl sulfates, more preferably the C_{11}-C_{15} branched chain alkyl sulfates and the C_{12}-C_{14} linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_{10}-C_{18} alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C_{11}-C_{18}, most preferably C_{11}-C_{15} alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C_5-C_{20} linear alkylbenzene sulfonates, alkyl ester sulfonates, C_6-C_{22} primary or secondary alkane sulfonates, C_6-C_{24} olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_20)_x\ CH_2C00^-M^+$ wherein R is a C_6 to C_{18} alkyl group, x ranges from O to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula $R\text{-}CON\ (R^1)\ CH_2\ COOM$, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Alkoxylated nonionic surfactant

A preferred additional surfactant in accord with the detergent composition of the invention is a nonionic surfactant present at a level of from 0.1% to 20%, more preferably from 0.2% to 10% by weight, most preferably from 0.5% to 5% by weight of the detergent composition.

Essentially any alkoxylated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

Preferred alkoxylated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic alkoxylated alcohol surfactant

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein : R1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C1-C4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R_2 is a C_5-C_{31} hydrocarbyl, preferably straight-chain C_5-C_{19} alkyl or alkenyl, more preferably straight-chain C_9-C_{17} alkyl or alkenyl, most preferably straight-chain C_{11}-C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a

linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

A preferred nonionic polyhydroxy fatty acid amide surfactant for use herein is a C_{15}-C_{17} alkyl N-methyl glucamide. The ratio of polyhydroxy fatty acid amide to cationic ester surfactant is preferably between 1:1 to 1:8, more preferably 1:2.5. It has been found that such surfactant systems are able to reduce 'lime soap' formation and deposition of encrustation on the fabric.

Nonionic fatty acid amide surfactant

Suitable fatty acid amide surfactants include those having the formula: $R^6CON(R^7)_2$ wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and -$(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

Preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)t(glycosyl)_x$$

wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10}-C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C_6-C_{18} hydrocarbyl group, each R^1 is typically C_1-C_3 alkyl, and R^2 is a C_1-C_5 hydrocarbyl group. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Cationic surfactants

Additional cationic surfactants can also be used in the detergent compositions herein. Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C_6-C_{16}, preferably C_6-C_{10} N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Water-soluble builder compound

The detergent compositions of the present invention preferably contain a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more that two carbon atoms, borates, phosphates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be momomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No.

1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

In a highly preferred aspect of the invention a means is also provided for delaying the release to a wash solution of the preferred water soluble builder component relatively to the release of the cationic ester surfactant. Said means can comprise equivalents of any of the delayed release means herein described for achieving the delayed release of the alkalinity system or species, described hereinbefore.

Partially soluble or insoluble builder compound

The detergent compositions of the present invention may contain a partially soluble or insoluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

Examples of largely water insoluble builders include the sodium aluminosilicates.

Suitable aluminosilicate zeolites have the unit cell formula $Na_z[(AlO_2)_z(SiO_2)y]$. xH_2O wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula

$Na_{12}[AlO_2)_{12}(SiO_2)_{12}]. xH_2O$

wherein x is from 20 to 30, especially 27. Zeolite X has the formula $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]. 276\ H_2O$.

Another preferred builder material is a crystalline layered silicate, preferably a crystalline δ-layered silicate, and most preferably the crystalline δ-layered silicate is a crystalline δ-layered sodium silicate with the general formula

$$NaMSi_xO_{2+1}.yH_2O$$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. Herein, x in the general formula above preferably has a value of 2, 3 or 4 and is preferably 2. The most preferred material is δ-$Na_2Si_2O_5$, available from Hoechst AG as NaSKS-6.

The crystalline layered silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionisable material. The solid, water-soluble ionisable material is selected from organic acids, organic and inorganic acid salts and mixtures thereof. Most preferably this material contains citric acid.

The Applicants have found that deposition onto the fabric in the wash of inorganic (insoluble) encrustation, for example caused by reaction of builder material such as zeolite and crystalline layered silicate with alkali metal and earth alkali metal ions, causing the hardness of the water, can be reduced by the cationic ester surfactants in accord with the present invention. The cationic ester surfactants facilitate suspension of the inorganic encrustation, thereby reducing the deposition of these inorganic materials onto the fabric. Two mechanisms are believed to be responsible therefor. Firstly, the interaction of the cationically charged ester surfactants with the negatively charged fabric surface can modify the fabric surface, which reduces deposition of inorganic encrustation onto the fabric surface. Secondly, the interaction of the cationically charged ester surfactants with anionically charged deposited builder material (such as zeolite and crystalline layered silicate) can facilitate the suspension of the deposited builder material, which reduces the fabric encrustation.

Organic peroxyacid bleaching system

A preferred feature of detergent compositions of the invention is an organic peroxyacid bleaching system. In one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of

hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches. In an alternative preferred execution a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Inorganic perhydrate bleaches

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the alkali metal, preferably sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material, such as described in the section 'delayed release-means'. Coatings can also be used to provide better storage stability for the perhydrate salt in the granular product. Suitable coatings therefor comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate is an addition compound having a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

In a preferred aspect of the present invention a means is provided to delay the release to a wash solution of the preferred inorganic perhydrate salts, relatively to the release of the cationic ester surfactant. Said means can comprise equivalents of any of the delayed release means herein described for achieving the delayed release of the alkalinity system or species, described hereinbefore.

Peroxyacid bleach precursors

Peroxyacid bleach precursors (bleach activators) are preferred peroxyacid sources in accord with the invention. Peroxyacid bleach precursors are normally incorporated at a level of from 0.5% to 20% by weight, more preferably from 2% to 10% by weight, most preferably from 3% to 5% by weight of the compositions.

Suitable peroxyacid bleach precursors typically contain one or more N- or O- acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1586789.

Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386. The acylation products of sorbitol, glucose and all saccharides with benzoylating agents and acetylating agents are also suitable.

Specific O-acylated precursor compounds include 2,3,3-tri-methyl hexanoyl oxybenzene sulfonates, benzoyl oxybenzene sulfonates, nonanoyl-6-amino caproyl oxybenzene sulfonates, monobenzoyltetraacetyl glucose benzoyl peroxide and cationic derivatives of any of the above, including the alkyl ammonium derivatives and pentaacetyl glucose. Phthalic anhydride is a suitable anhydride type precursor.

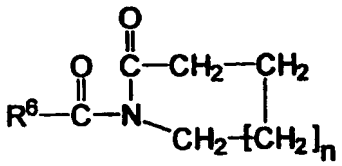
Specific cationic derivatives of the O-acyl precursor compounds include 2-(N,N,N-trimethyl ammonium) ethyl sodium 4-sulphophenyl carbonate chloride, and any of the alkyl ammonium derivatives of the benzoyl oxybenzene sulfonates including the 4-(trimethyl ammonium) methyl derivative.

Useful N-acyl compounds are disclosed in GB-A-855735, 907356 and GB-A-1246338.

Preferred precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine, N-benzoyl substituted ureas and the N-,N,N^1N^1 tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred. Preferably, the tetraacetyl ethylene diamine has a compressed particle structure, achieved by mechanically compression, to delay the desolving of the particles into the wash solution.

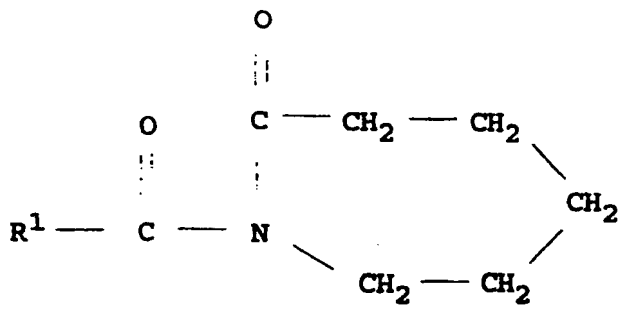
N-acylated precursor compounds of the lactam class are disclosed generally in GB-A-955735. Preferred materials comprise the caprolactams and valerolactams.

Suitable N-acylated lactam precursors have the formula:



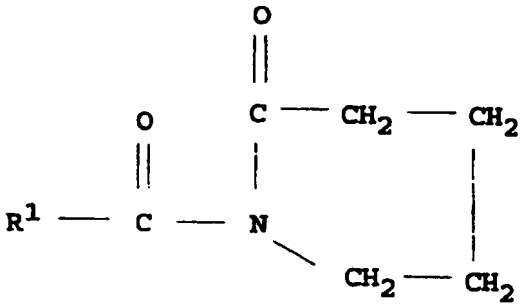
wherein n is from 0 to 8, preferably from 0 to 2, and R^6 is H, an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbons, or a substituted phenyl group containing from 6 to 18 carbon atoms

Suitable caprolactam bleach precursors are of the formula:



wherein R^1 is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms, most preferably R^1 is phenyl.

Suitable valero lactams have the formula:



wherein R^1 is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms. In highly preferred embodiments, R^1 is selected from phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

The most preferred materials are those which are normally solid at $<30°C$, particularly the phenyl derivatives, ie. benzoyl valerolactam, benzoyl caprolactam and their substituted benzoyl analogues such as chloro, amino alkyl, alkyl, aryl and alkoxy derivatives.

Caprolactam and valerolactam precursor materials wherein the R^1 moiety contains at least 6, preferably from 6 to 12, carbon atoms provide peroxyacids on perhydrolysis of a hydrophobic character which afford nucleophilic and body soil clean-up. Precursor compounds wherein R^1

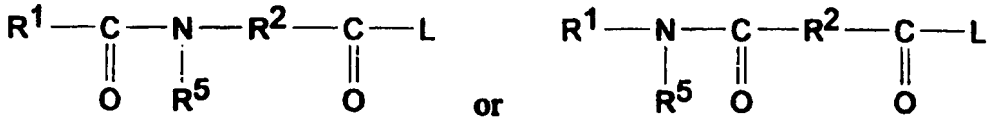
comprises from 1 to 6 carbon atoms provide hydrophilic bleaching species which are particularly efficient for bleaching beverage stains. Mixtures of 'hydrophobic' and 'hydrophilic' caprolactams and valero lactams, typically at weight ratios of 1:5 to 5:1, preferably 1:1, can be used herein for mixed stain removal benefits.

Highly preferred caprolactam and valerolactam precursors include benzoyl caprolactam, nonanoyl capro-lactam, benzoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl caprolactam, 3,5,5-trimethylhexanoyl valerolactam, octanoyl caprolactam, octanoyl valerolactam, decanoyl caprolactam, decanoyl valerolactam, undecenoyl caprolactam, undecenoyl valerolactam, (6-octanamidocaproyl)oxybenzene-sulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)-oxybenzenesulfonate, and mixtures thereof. Examples of highly preferred substituted benzoyl lactams include methylbenzoyl caprolactam, methylbenzoyl valerolactam, ethylbenzoyl caprolactam, ethylbenzoyl valerolactam, propylbenzoyl caprolactam, propylbenzoyl valerolactam, isopropylbenzoyl caprolactam, isopropylbenzoyl valerolactam, butylbenzoyl caprolactam, butylbenzoyl valerolactam, tert-butylbenzoyl caprolactam, tert-butylbenzoyl valerolactam, pentylbenzoyl caprolactam, pentylbenzoyl valerolactam, hexylbenzoyl caprolactam, hexylbenzoyl valerolactam, ethoxybenzoyl caprolactam, ethoxybenzoyl valerolactam, propoxybenzoyl caprolactam, propoxybenzoyl valerolactam, isopropoxybenzoyl caprolactam, isopropoxybenzoyl valerolactam, butoxybenzoyl caprolactam, butoxybenzoyl valerolactam, tert-butoxybenzoyl caprolactam, tert-butoxybenzoyl valerolactam, pentoxybenzoyl caprolactam, pentoxybenzoyl valerolactam, hexoxybenzoyl caprolactam, hexoxybenzoyl valerolactam, 2,4,6-trichlorobenzoyl caprolactam, 2,4,6-trichlorobenzoyl valerolactam, pentafluorobenzoyl caprolactam, pentafluorobenzoyl valerolactam, dichlorobenzoyl caprolactam, dimethoxybenzoyl caprolactam, 4-chlorobenzoyl caprolactam, 2,4-dichlororbenzoyl caprolactam, terephthaloyl dicaprolactam, pentafluorobenzoyl caprolactam, pentafluorobenzoyl valerolactam, dichlorobenzoyl valerolactam, dimethoxybenzoyl valerolactam, 4-chlorobenzoyl valerolactam, 2,4-dichlororbenzoyl valerolactam, terephthaloyl divalerolactam, 4-

nitrobenzoyl caprolactam, 4-nitrobenzoyl valerolactam, and mixtures thereof.

Suitable imidazoles include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-containing peroxyacid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Another preferred class of peroxyacid bleach activator compounds are the amide substituted compounds of the following general formulae:

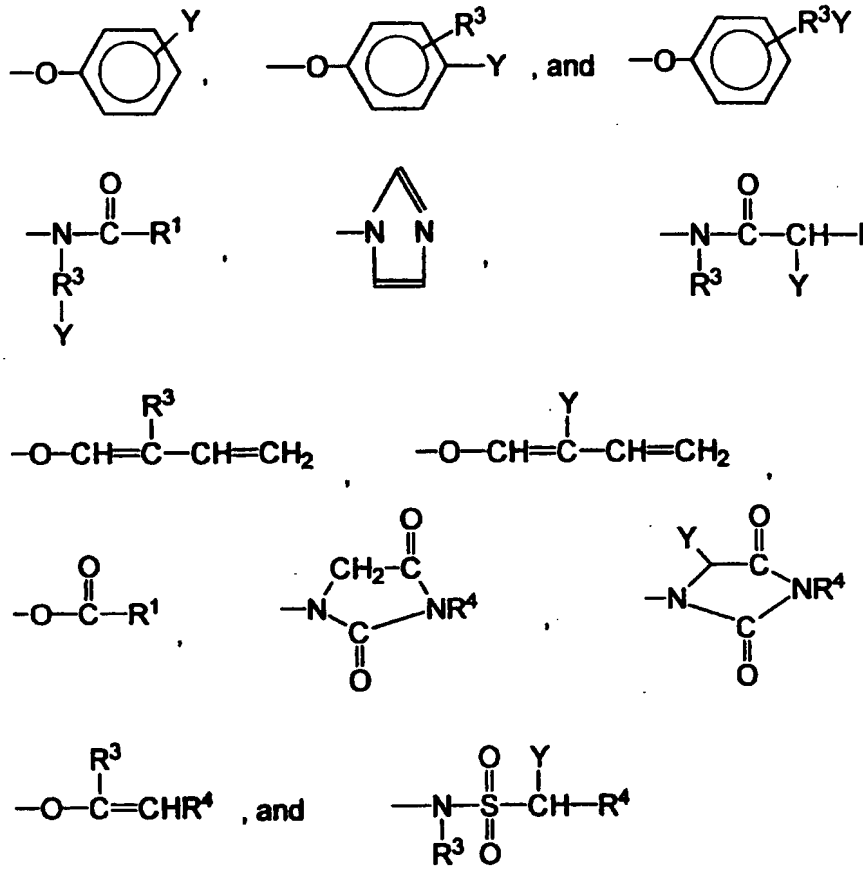


wherein R^1 is an aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

The L group must be sufficiently reactive for the reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition. These characteristics are generally paralleled by the pKa of the conjugate acid of the leaving group, although exceptions to this convention are known. Ordinarily, leaving groups that exhibit such

behavior are those in which their conjugate acid has a pKa in the range of from 4 to 13, preferably from 6 to 11 and most preferably from 8 to 11.

Preferred bleach precursors are those wherein R^1, R^2 and R^5 are as defined for the amide substituted compounds and L is selected from the group consisting of:



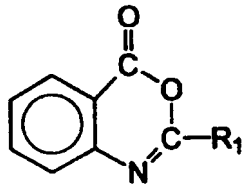
and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3, and Y is H or a solubilizing group.

The preferred solubilizing groups are $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and $O<--N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator.

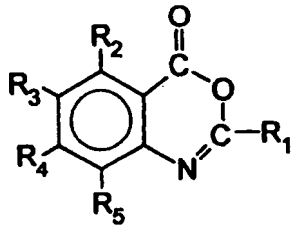
Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion. It should be noted that bleach activators with a leaving group that does not contain a solubilizing groups should be well dispersed in the bleaching solution in order to assist in their dissolution.

Preferred examples of bleach activators of the above formulae include (6-octanamidocaproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfo-nate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof.

Other preferred precursor compounds include those of the benzoxazin-type, having the formula:

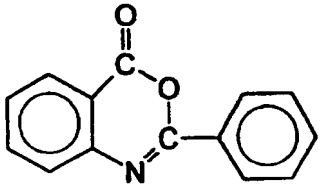


including the substituted benzoxazins of the type



wherein R_1 is H, alkyl, alkaryl, aryl, arylalkyl, and wherein R_2, R_3, R_4, and R_5 may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxyl, amino, alkyl amino, $COOR_6$ (wherein R_6 is H or an alkyl group) and carbonyl functions.

An especially preferred precursor of the benzoxazin-type is:



Bleach catalyst

The detergent compositions optionally contain a transition metal containing bleach catalyst. One suitable type of bleach catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $Mn^{IV}_2(u\text{-}O)_3$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(PF_6)_2$, $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_2$; $Mn^{IV}_4(u\text{-}O)_6$(1,4,7-triazacyclononane)$_4$-$(ClO_4)_2$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2$-(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)$(OCH_3)_3$-(PF_6). Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $N_4Mn^{III}(u\text{-}O)_2Mn^{IV}N_4)^+$ and $[Bipy_2Mn^{III}(u\text{-}O)_2Mn^{IV}bipy_2]$-$(ClO_4)_3$.

Further suitable bleach catalysts are described, for example, in European patent application No. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Heavy metal ion sequestrant

The detergent compositions of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β-alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are alos suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N-N'-diglutaric acid (EDDG) and 2-hydroxypropylenediamine-N-N'-disuccinic acid (HPDDS) are also suitable.

Enzyme

Another preferred ingredient useful in the detergent compositions is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally

incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α-amylases obtained from a special strain of B licheniformis, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Preferably the detergent composition in accordance with the present invention contains a lipolytic enzyme. It has been found that the cationic ester surfactant enhances the performance of the lipolytic enzyme. Two mechanisms are believed to be responsible for the improved enzyme performance. Firstly, the fatty acids, which are formed by the enzymatic reaction of the lipolytic enzymes with triglycerides contained in the greasy or oily soils, will be removed from the fabric surface by the cationic ester surfactant. This will facilitate the 'access' by the enzymes to the greasy stains/ soils during the washing process. Secondly, the removal of fatty acids from the fabric surface by the cationic ester surfactant will reduce the formation and deposition onto the fabric of 'lime soap', formed through reaction of fatty acids with calcium ions of the hardness of the water. This will also facilitate the 'access' by the enzymes to the greasy stains/ soils on the fabric surface.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.01% to 5% by weight, preferably 0.1% to 2% by weight, most preferably from 0.1% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989. A highly preferred lipase, which is also obtained via Humicola lanuginosa, is a lipase known as Lipase Ultra SP514 (trade name), also available from NOVO Industri A/S.

Organic polymeric compound

Organic polymeric compounds are preferred additional components of the detergent compositions in accord with the invention, and are preferably present as components of any particulate components where they may act such as to bind the particulate component together. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably

from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 100,000, especially 40,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Suds suppressing system

The detergent compositions of the invention, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts. A disadvantage associated with such fatty acid antifoams is their tendency to interact with any Ca^{++} or Mg^{++} ion present in the wash solution, to form insoluble 'lime soaps', which can deposit on the fabric in the wash. It has now been found that this problem can be reduced by the presence of cationic ester surfactants. The cationic ester surfactant interacts with the formed 'lime soaps', thereby suspending them in the wash solution, and thus reducing the deposition of the formed 'lime soaps' on the fabric in the wash.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of

monovalent alcohols, aliphatic C_{18}-C_{40} ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises

(a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination

(i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and

(ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

(b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;

(c) an inert carrier fluid compound, most preferably comprising a C_{16}-C_{18} ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

Clay softening system

The detergent compositions may contain a clay softening system comprising a clay mineral compound and optionally a clay flocculating agent.

The clay mineral compound is preferably a smectite clay compound. Smectite clays are disclosed in the US Patents No.s 3,862,058, 3,948,790, 3,954,632 and 4,062,647. European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe suitable organic polymeric clay flocculating agents.

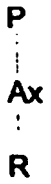
Polymeric dye transfer inhibiting agents

The detergent compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

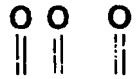
The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidonepolymers or combinations thereof.

a) Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :

(I) 

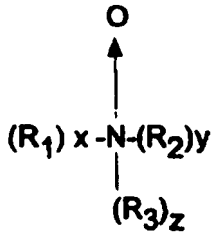
wherein P is a polymerisable unit, and



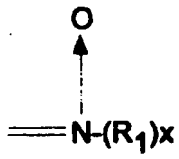
A is NC, CO, C, -O-, -S-, -N-; x is O or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



or



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group

such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises the polyamine N-oxides having the general formula (I) wherein R is an aromatic,heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

The polyamine N-oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Suitable herein are coploymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

c) Polyvinylpyrrolidone

The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially vailable from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

d) Polyvinyloxazolidone

The detergent compositions herein may also utilize polyvinyloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinyloxazolidones have an average molecular weight of from 2,500 to 400,000.

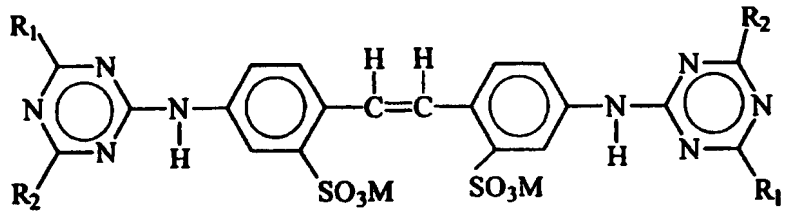
e) Polyvinylimidazole

The detergent compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000.

Optical brightener

The detergent compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid

and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Cationic fabric softening agents

Cationic fabric softening agents can also be incorporated into compositions in accordance with the present invention. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

Cationic fabric softening agents are typically incorporated at total levels of from 0.5% to 15% by weight, normally from 1% to 5% by weight.

Other optional ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

pH of the compositions

The present compositions preferably have a pH measured as a 1% solution in distilled water of at least 9.0, preferably from 9.0 to 11.5, most preferably from 9.5 to 10.5.

Form of the compositions

The compositions in accordance with the invention can take a variety of physical forms including granular, tablet, bar and liquid forms. The compositions are particularly the so-called concentrated granular detergent compositions adapted to be added to a washing machine by means of a dispensing device placed in the machine drum with the soiled fabric load.

The mean particle size of the components of granular compositions in accordance with the invention should preferably be such that no more that 5% of particles are greater than 1.7mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

The bulk density of granular detergent compositions in accordance with the present invention typically have a bulk density of at least 600 g/litre, more preferably from 650 g/litre to 1200 g/litre. Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall

height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk density in g/litre. Replicate measurements are made as required.

Surfactant agglomerate particles

The surfactant system herein is preferably present in granular compositions in the form of surfactant agglomerate particles, which may take the form of flakes, prills, marumes, noodles, ribbons, but preferably take the form of granules. The most preferred way to process the particles is by agglomerating powders (e.g. aluminosilicate, carbonate) with high active surfactant pastes and to control the particle size of the resultant agglomerates within specified limits. Such a process involves mixing an effective amount of powder with a high active surfactant paste in one or more agglomerators such as a pan agglomerator, a Z-blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands, and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050, Germany. Most preferably a high shear mixer is used, such as a Lodige CB (Trade Name).

The Applicants have found that the flow properties of cationic ester surfactant-containing granules be improved by the addition of a desiccant during the granulation process. The desiccant absorbs water during the granulation process and also absorbs atmospheric moisture during the storage of the finished product. Such absorbance of atmospheric moisture also improves the stability of the cationic ester surfactant which can hydrolyse in moisturous conditions. Preferred desiccants are (anhydrous) $MgSO_4$ and dried sodium aluminosilicates, such as Zeolite A, and silicates.

The Applicants have also found that stability of cationic ester surfactant-containing particles can be improved when the level of heavy metal ions in the particle making process is reduced, since heavy metal ions can catalyse the hydrolysis of the cationic ester surfactants. This can be achieved by limiting the possible contact of cationic ester surfactants and heavy metal ions throughout the particle making process, for example through the use of vessels, which are free of or substantially free of heavy metal ions, such as glass vessels or synthetic plastic lined vessels. The stability of cationic ester surfactant containing particles can also be improved by addition of trace levels of heavy metal ion sequestrants

during the particle making process or by spraying the heavy metal ion sequestrants onto the particles once formed. Suitable heavy metal ion sequestrants, which can be sprayed onto or added to the particles in trace levels up to 3% by weight of the particles, include any of those described herein. Other suitable sequestering agents include certain organic polymeric compounds, including acrylic/ maleic acid copolymers.

Surfactant particle micro-pastillation

The cationic ester surfactants may be included in the form of micro-pastilles, formed by a so called 'pastillation process'. A preferred process for the manufacture of detergent micro-pastilles from a surfactant paste which is substantially in the solid phase at temperatures of 25°C and below, comprises the steps of :
(i) mixing the surfactant paste at a temperature above its softening point, the surfactant paste comprising at least 50% by weight of nonionic surfactant;
(ii) forming the molten surfactant paste into drops on a cooling belt;
(iii) forming solid pastilles by cooling the drops of molten surfactant paste; and
(iv) removing solidified pastilles from the cooling belt.

In the process, the molten surfactant paste is preferably formed into drops by a continuous rotary drop former comprising outer and inner coaxial cylinders, both cylinders comprising a series of openings, at least one of the cylinders being rotatable. The molten surfactant drops are conveniently formed on a continuous steel cooling belt and, optionally, cooled by spraying a cooling liquid on to the opposite side of the belt to the side on which the drops are formed.

The micro-pastilles characteristically have a generally rounded surface profile and at least one substantially planar surface.

To improve the flow properties of the granules and to improve the surfactant stability, the particle size of the granules should be controlled so as to achieve the most ideal size. Therefore, the surfactant paste is

preferably undercooled before the melting process step and a crystal growth carrier such as choline chloride can be added. Hereby will be achieved that the granules, tablets or pastilles will have the preferred size.

Preferably a so called 'dusting agent' is added to the micro-pastilles, to avoid product caking and to improve the flow properties and surfactant stability. Preferably a hydrophobic dusting agent is, such as hydrophobic silica, is employed.

To improve the flow properties of the granules during the process (i.e. the flow from one process step/ vessel/ container to an other) the powder should be essentially free from water or moisture and therefore a desiccant is preferably added during the micro-pastillation process.

Particle morphology

The cationic ester surfactant containing particles or micro-pastilles formed during the granulation process or the pastillation process, are susceptible to decomposition when in alkaline, under moisturous conditions. The particle or micro-pastille stability however can be improved, when the particle has a specific morphology, which can been defined by a morphology index MI. The morphology index can be calculated with the following formula:

$$MI = (0.0448 \times CV) + (3.61 \times 10^6 / d^3)$$

wherein CV is the coefficient of variation of weight average particle size distribution and d is the weight mean average particle size in microns. Preferably MI is less then 0.06, more preferably less than 0.04 and most preferably less than 0.03.

Laundry washing method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective

amount of the detergent composition it is meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

In a preferred use aspect a dispensing device is employed in the washing method. The dispensing device is charged with the detergent product, and is used to introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.

Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water.

To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use with the composition of the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred

dispensing devices for use with granular laundry products which are of a type commonly know as the "granulette". Another preferred dispensing device for use with the compositions of this invention is disclosed in PCT Patent Application No. WO94/11562.

Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

Packaging for the compositions

Commercially marketed executions of the bleaching compositions can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A

preferred packaging execution is described in European Application No. 94921505.7.

Alkalinity requirement and relative delay of alkalinity release

In the following Examples 1 to 9 an alkalinity system is provided. In each example a means is provided for delaying the release to a wash solution of the alkalinity system, relatively to the cationic ester surfactant. The means for delaying the alkalinity release is such that the time to achieve a concentration that is 50% of the ultimate concentration of the cationic ester surfactant is at least 120 seconds less than the time to achieve a concentration that is 50% of the ultimate concentration of the alkalinity system, as described herein in the T50 test method.

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	:	Sodium linear C_{12} alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
C45AS	:	Sodium C_{14}-C_{15} linear alkyl sulfate
CxyEzS	:	Sodium C_{1x}-C_{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
C45E7	:	A C_{14-15} predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
C25E3	:	A C_{12-15} branched primary alcohol condensed with an average of 3 moles of ethylene oxide
C25E5	:	A C_{12-15} branched primary alcohol condensed with an average of 5 moles of ethylene oxide
CEQ I	:	$R_1COOCH_2CH_2.N^+(CH_3)_3$ with R_1 = C_{11}-C_{13}
CEQ II	:	$R_1COOCH_2CH_2CH_2N^+(CH_3)_3$ with R_1 = C_{11}-C_{13}

CEQ III	:	$R_1COO\ CH_2\ CH_2\ N^+(CH_3)_2(CH_2CH_2OH)$ with $R_1 = C_{11}$-C_{13}
CEQ IV	:	$R_1\ COOCH_2CH_2\ N^+\ (CH_3CH_2)_2(CH_3)$ with $R_1 = C_{11}$-C_{13}
QAS	:	$R_2.N^+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_{12} - C_{14}$
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
TFAA	:	C_{16}-C_{18} alkyl N-methyl glucamide
TPKFA	:	C12-C14 topped whole cut fatty acids
STPP	:	Anhydrous sodium tripolyphosphate
Zeolite A	:	Hydrated Sodium Aluminosilicate of formula $Na_{12}(A10_2SiO_2)_{12}.\ 27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers
NaSKS-6	:	Crystalline layered silicate of formula δ -$Na_2Si_2O_5$
Citric acid	:	Anhydrous citric acid
Carbonate	:	Anhydrous sodium carbonate with a particle size between 200μm and 900μm
Carbonate, amorphous	:	Amorphous sodium carbonate with a particle size between 200μm and 900μm
Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
Bicarbonate amorphous	:	Amorphous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
Silicate	:	Amorphous Sodium Silicate (SiO_2:Na_2O; 2.0 ratio)
Sodium sulfate	:	Anhydrous sodium sulfate
Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425μm and 850 μm
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
CMC	:	Sodium carboxymethyl cellulose

Protease	:	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
Alcalase	:	Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
Cellulase	:	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
Amylase	:	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
Lipase	:	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
Endolase	:	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
PB4	:	Sodium perborate tetrahydrate of nominal formula $NaBO_2.3H_2O.H_2O_2$
PB1	:	Anhydrous sodium perborate bleach of nominal formula $NaBO_2.H_2O_2$
Percarbonate	:	Sodium Percarbonate of nominal formula $2Na_2CO_3.3H_2O_2$
Percarbonate (slow release particle	:	Anhydrous sodium percarbonate bleach coated with a coating of sodium silicate (Si_2O:Na_2O ratio = 2:1) at a weight ratio of percarbonate to sodium silicate of 39:1
NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt.
TAED	:	Tetraacetylethylenediamine
DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
Photoactivated bleach	:	Sulfonated Zinc Phthlocyanine encapsulated in dextrin soluble polymer
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.

HEDP	:	1,1-hydroxyethane diphosphonic acid
PVNO	:	Polyvinylpyridine N-oxide
PVPVI	:	Copolymer of polyvinylpyrolidone and vinylimidazole
SRP 1	:	Sulfobenzoyl end capped esters with oxyethylene oxy and terephtaloyl backbone
SRP 2	:	Diethoxylated poly (1, 2 propylene terephtalate) short block polymer
Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

In the following Examples all levels are quoted as % by weight of the composition:

Example 1

The following laundry detergent compositions A to F were prepared in accord with the invention:

	A	B	C	D	E	F
LAS	8.0	8.0	8.0	8.0	8.0	8.0
C25E3	3.4	3.4	3.4	3.4	3.4	3.4
CEQ I	-	0.8	-	2.0	-	0.7
CEQ II	6.0	0.5	-	0.7	2.0	0.8
QAS	-	-	0.8	-	-	0.8
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate, amorphous	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sodium sulfate	26.1	26.1	26.1	26.1	26.1	26.1
PB4	5.0	5.0	6.0	6.0	4.0	4.0
Percarbonate slow release particle	4.0	4.0	3.0	3.0	5.0	5.0
TAED	1.5	1.5.	1.5	1.5	1.5	1.5
DETPMP	0.25	0.25	0.25	0.25	0.25	0.25

HEDP	0.3	0.3	0.3	0.3	0.3	0.3
Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.1	0.1	0.1	0.1
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

Example 2

The following granular laundry detergent compositions G to I of bulk density 750 g/litre were prepared in accord with the invention:

	G	H	I
LAS	5.25	5.61	4.76
TAS	1.25	1.86	1.57
C45AS	-	2.24	3.89
C25AE3S	-	0.76	1.18
C45E7	3.25	-	5.0
C25E3	-	5.5	-
CEQ II	0.8	-	2.8
CEQ III	0.4	2.0	0.5
STPP	19.7	-	-
Zeolite A	-	19.5	19.5
NaSKS-6/citric acid (79:21)	-	10.6	10.6
Carbonate, amorphous	6.1	21.4	21.4
Bicarbonate, amorphous	-	2.0	2.0
Silicate	6.8	-	-

Sodium sulfate	39.8	-	14.3
Percarbonate slow release particle	5.0	12.7	8.0
TAED	0.5	3.1	-
DETPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
Protease	0.26	0.85	0.85
Lipase	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28
Amylase	0.1	0.1	0.1
MA/AA	0.8	1.6	1.6
CMC	0.2	0.4	0.4
Photoactivated bleach (ppm)	15 ppm	27 ppm	27 ppm
Brightener 1	0.08	0.19	0.19
Brightener 2	-	0.04	0.04
Perfume	0.3	0.3	0.3
Silicone antifoam	0.5	2.4	2.4
Minors/misc to 100%			

Example 3

The following detergent formulations, according to the present invention were prepared, where J is a phosphorus-containing detergent composition, K is a zeolite-containing detergent composition and L is a compact detergent composition:

	J	K	L
Blown Powder			
STPP	24.0	-	24.0
Zeolite A	-	24.0	-
C45AS	9.0	6.0	13.0
MA/AA	2.0	4.0	2.0
LAS	6.0	8.0	11.0
TAS	2.0	-	-
CEQ I	-	2.0	-
CEQ II	-	-	2.0
CEQ III	2.0	-	-
Silicate	7.0	3.0	3.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DTPMP	0.4	0.4	0.2
Spray On			
C45E7	2.5	2.5	2.0
C25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Carbonate, amorphous	6.0	13.0	15.0
Percarbonate slow release particle	18.0	18.0	10.0
PB1	4.0	4.0	0
TAED	3.0	3.0	1.0
Photoactivated bleach	0.02	0.02	0.02
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4

Amylase	0.25	0.30	0.15
Dry mixed sodium sulfate	3.0	3.0	5.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	630	670	670

Example 4

The following nil bleach-containing detergent formulations of particular use in the washing of colored clothing, according to the present invention were prepared:

	M	N	O
Blown Powder			
CEQ II	0.5	0.5	0.5
CEQ III	1.0	1.5	0.5
CEQ IV	0.5	1.5	2.0
Zeolite A	15.0	15.0	-
Sodium sulfate	0.0	5.0	-
LAS	3.0	3.0	-
DTPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray On			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0

Dry additives			
MA/AA	-	-	3.0
NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate, amorphous	7.0	3.0	5.0
Carbonate, amorphous	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Alcalase	0.5	0.3	0.9
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	9.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	700	700	700

Example 5

The following detergent formulations, according to the present invention were prepared:

	P	Q	R	S
CEQ III	0.4	-	3.5	1.5
CEQ IV	1.5	2.4	-	1.5
LAS	20.0	14.0	24.0	22.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C25E5/C45E7	-	2.0	-	0.5
C45E3S	-	2.5	-	-
STPP	30.0	18.0	30.0	22.0
Silicate	9.0	5.0	10.0	8.0
Carbonate, amorphous	13.0	7.5	-	5.0
Bicarbonate	-	7.5	-	-
DTPMP	0.7	1.0	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Protease	0.8	1.0	0.5	0.5
Amylase	0.8	0.4	-	0.25
Lipase	0.2	0.1	0.2	0.1
Cellulase	0.15	0.05	-	-
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener 1	0.2	0.2	0.08	0.2
Percarbonate slow release particle	6.0	2.0	-	-
PB1	-	-	2.0	3.0
NOBS	2.0	1.0	-	-
Balance (Moisture and Miscellaneous)	100	100	100	100

Example 6

The following detergent formulations, according to the present invention were prepared:

	T	U	V
Blown Powder			
Zeolite A	30.0	22.0	6.0
Sodium sulfate	19.0	5.0	7.0
MA/AA	3.0	3.0	6.0
LAS	14.0	12.0	22.0
C45AS	8.0	7.0	7.0
CEQ II	-	0.4	2.5
CEQ IV	1.5	1.5	0.5
Silicate	-	1.0	5.0
Soap	-	-	2.0
Brightener 1	0.2	0.2	0.2
Carbonate, amorphous	8.0	16.0	20.0
DTPMP	-	0.4	0.4
Spray On			
C45E7	1.0	1.0	1.0
Dry additives			
PVPVI/PVNO	0.5	0.5	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.1	0.1	0.1
Cellulase	0.1	0.1	0.1
NOBS	-	6.1	4.5
PB1	1.0	5.0	6.0
Sodium sulfate	-	6.0	-
Balance (Moisture and Miscellaneous)	100	100	100

Example 7

The following high density and bleach-containing detergent formulations, according to the present invention were prepared:

	W	X	Y
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sodim sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
CEQ II	0.5	0.5	-
CEQ III	0.9	1.2	2.5
DTPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
Citrate	5.0	-	2.0
Bicarbonate, amorphous	-	3.0	-
Carbonate, amorphous	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	7.0	3.5	5.0
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4

Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Percarbonate slow release particle	7.0	3.5	5.0
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	850	850	850

Example 8

The following high density detergent formulations, according to the present invention were prepared:

	Z	AA
Agglomerate		
C45AS	11.0	14.0
CEQ IV	0.8	2.2
Zeolite A	15.0	6.0
Carbonate, amorphous	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DTPMP	0.4	0.4
Spray On		
C25E5	5.0	5.0
Perfume	0.5	0.5
Dry Adds		
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	3.0	1.0
TAED	5.0	7.0
Percarbonate	10.0	10.0
Percarbonate slow release particle	10.0	10.0
SRP 1	0.3	0.3
Protease	1.4	1.4
Lipase	0.4	0.4
Cellulase	0.6	0.6
Amylase	0.6	0.6
Silicone antifoam	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-
Balance (Moisture and Miscellaneous)	100	100
Density (g/litre)	850	850

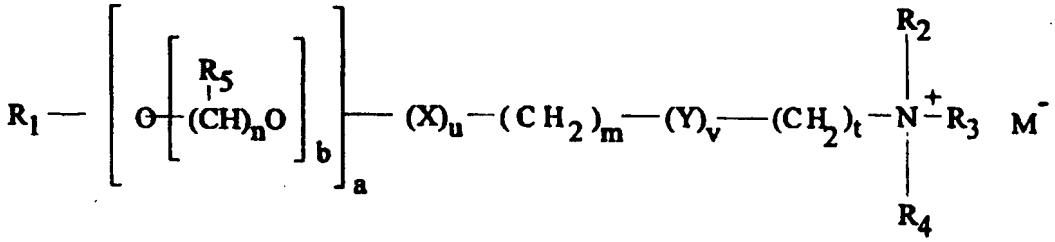
WHAT IS CLAIMED IS:

1. A detergent composition containing
   (a) a cationic ester surfactant; and
   (b) an alkalinity system,

wherein a means is provided for delaying the release to a wash solution of said alkalinity system relative to the release of said cationic ester surfactant such that in the T50 test method herein described the time to achieve a concentration that is 50% of the ultimate concentration of said cationic ester surfactant is at least 120 seconds less than the time to achieve a concentration that is 50% of the ultimate concentration of said alkalinity system.

2. A detergent composition according to Claim 1, wherein said means is a means delaying the release to a wash solution of said alkalinity system relative to the release of said cationic ester surfactant such that in the T50 test method herein described the time to achieve a concentration that is 50% of the ultimate concentration of said cationic ester surfactant is at least 300 seconds less than the time to achieve a concentration that is 50% of the ultimate concentration of said alkalinity system.

3. A detergent composition according to any of Claims 1 or 2, wherein said cationic ester surfactant is selected from those having the formula:

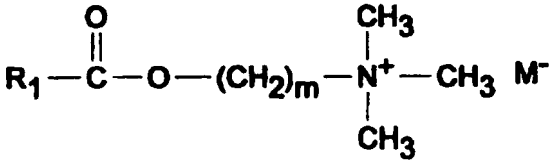


wherein R_1 is a C_5-C_{31} linear or branched alkyl, alkenyl or alkaryl chain or M^-. $N^+(R_6R_7R_8)(CH_2)_S$; X and Y, independently, are selected from the group consisting of COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCO,

OCOO, OCONH or NHCOO group; R_2, R_3, R_4, R_6, R_7, and R_8 are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl, hydroxy-alkenyl and alkaryl groups having from 1 to 4 carbon atoms; and R_5 is independently H or a C_1-C_3 alkyl group; wherein the values of m, n, s and t independently lie in the range of from 0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion.

4. A detergent composition according to Claim 3 wherein R_2, R_3 and R_4 are independently selected from the group consisting of C_1-C_3 alkyl and hydroxyalkyl groups.

5. A detergent composition according to Claim 3 wherein the cationic ester is selected from the choline esters having the formula:



wherein m is from 1 to 4 and R_1 is a C_{11}-C_{19} linear or branched alkyl chain.

6. A detergent composition according to any of Claims 1 to 5, wherein the cationic ester surfactant is present in an amount of from 0.1% to 20% by weight of the detergent composition.

7. A detergent composition according to any of Claims 1 to 6, wherein the cationic ester surfactant is present in an amount of from 0.5% to 5% by weight of the detergent composition.

8. A detergent composition according to any of Claims 1 to 7, wherein the alkalinity system is present in an amount of from 1% to 75% by weight of the detergent composition.

9. A detergent composition according to any of Claims 1 to 8, wherein the alkalinity system is present in an amount of from 10% to 40% by weight of the detergent composition.

10. A detergent composition according to any of Claims 1 to 9, wherein said alkalinity system comprises alkaline salts selected from the group consisting of alkali metal or alkaline earth carbonate, bicarbonate, hydroxide or silicate salts, crystalline layered silicate and any mixtures thereof.

11. A detergent composition according to any of the Claims 1 to 10, wherein said alkalinity system comprises alkaline salts selected from the group consisting of inorganic perhydrate salt.

12. A method of washing laundry in a domestic washing machine in which a dispensing device containing an effective amount of a solid detergent composition according to any of Claims 1 to 11 is introduced into the drum of the washing machine before the commencement of the wash, wherein said dispensing device permits progressive release of said detergent composition into the wash liquor during the wash.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/08233

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C11D 11/02, 1/62, 3/08, 3/10
US CL :510/315, 330, 334, 345, 443, 444, 504
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/315, 330, 334, 345, 443, 444, 504

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS
search terms: spray dried, spray drying, choline ester, cationic ester

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,321,157 A (HARRIS et al) 23 March 1982, column 15, line 29-column 16, line 19, column 18, lines 30-35, column 20, lines 56-61	1-5
X	US 4,321,165 A (SMITH et al) 23 March 1982, column 5, line 18-column 6, line 20, column 10, lines 49-55, column 14, lines 41-43 and 45-48.	1-5
X	US 4,255,273 A (SAKKAB) 10 March 1981, column 8, lines 24-67, column 62, lines 9-17, column 64, Table II.	1-5
X	US 4,240,920 A (DE LUQUE) 23 December 1980, column 7, line 53-column 8, line 52, column 10, lines 43-54, column 22, lines 1-9.	1-5

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 02 JULY 1997	Date of mailing of the international search report 24 SEP 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer JOHN R. HARDEE Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/08233

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,347,168 A (MURPHY et al) 31 August 1982, column 9, lines 16-20, column 11, lines 46-51, column 12, lines 43-45 and 48-51.	1-5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/08233

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 6-12
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.